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ORIGINAL ARTICLE

Implementation of chitosan inductively modified by γ-rays copolymerization with acrylamide in the decontamination of aqueous basic dye solution

R.O. Aly

National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt

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KEYWORDS

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Chitosan;
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Abstract The modification induced by gamma rays for the natural polymer, chitosan, was established using the monomer acrylamide. The hydrogel obtained was characterized using Fourier transform infrared spectroscopy and the thermal properties were investigated by thermogravimetric analysis (TGA). The effect of absorbed dose (kGy) and chitosan:acrylamide ratio on the gel % was studied. The impact of the polymerization variables was observed on the swelling % of the prepared hydrogel with water. The highest equilibrium degree of swelling of the prepared chitosan–AAm hydrogel, 380 g/g was predicted at 75% AAm and absorbed dose of 10 kGy for 97.7% gel. The removal of the basic blue dye (Astrazone Blue BG-200%) from aqueous solutions was discussed. The adsorption capacity of basic dye on chitosan–AAm increased from 24.5 to 47.2 mg/g by increasing pH from 4.0 to 9.0. The effect of pH, absorbed dose, chitosan:AAm ratio and the concentration of the dye on the effectiveness of the adsorption process was studied.
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1. Introduction

The hydrogel composed of chitosan/AAm has been found to be a good candidate as a supporting material for removal of some undesirable organic pollutants as well as basic blue dyes. Chitosan formed as a β-(1 → 4) linked polysaccharide made up of D-glucosamine residues [poly-β-(1–4)-D-glucosamine], is an *N*-deacetylated derivative of chitin, the second most abundant natural organic resource only next to cellulose on the earth (Juang and Shao, 2002). It is widely distributed in arthropods, crustaceans, fungi, and yeast (Chung et al., 2003). However, it is usually regarded as a waste. Since chitosan is biodegradable and non-toxic, recently many efforts have been made to pursue its applications, especially for wastewater treatment and sludge dewatering (Bratskaya et al., 2004; Divakaran and Pillai, 2004; Wibowo et al., 2007). Because of the inter- and intra-molecular hydrogen bonding, chitosan can be dissolved in only acidic solutions through the interaction between H^+ and $-NH_2$. This might accelerate its degradation and consequently reduce its flocculent efficiency (Biswal and Singh, 2004). In order to sort out this problem, a lot of work has been conducted on the

E-mail address: raoufokasha@yahoo.co.uk
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modification of chitosan (Kumar et al., 1999; Huang et al., 2000; Sashiwa et al., 2001, 2003; Masuko et al., 2005; Wibowo et al., 2005).

For a breakthrough in utilization, graft copolymerization onto chitosan introduces the desired properties and enlarges the field of potential applications by choosing various types of side chains. Such as grafting percentage and grafting efficiency. The graft copolymerized chitosans find its potential applications in the field of drug delivery, tissue engineering, antibacterial, biomedical, metal adsorption and dye removal. The abundant amino groups and hydroxyl groups in chitosan backbone could react with vinyl monomers under mild conditions (Navarro and Tatsumi, 2001; Sashiwa and Aiba, 2004; Zhou et al., 2007).

Studies were reported on graft polymerization of butyl acrylate onto chitosan by using γ-irradiation and revealed that increasing grafting percentage was observed when the monomer concentration and the total irradiation dose were increased (Yu et al., 2004; Jayakumara et al., 2005). Others have also reported the radiation grafting of chitosan with *N,N* dimethylaminiethylmethacrylate (DMAEMA) Yilmaz et al., 2007. A flexible polyacrylamide grafted onto rigid polysaccharide backbones increases the probability for the flocculent to approach the contaminant particles, and thus improves the flocculent ability of polysaccharide and has been extensively used for wastewater treatment and sludge dewatering (Singh et al., 1995, 2000).

Research groups have taken into consideration to study of the chemical nature of crosslinker and showed that it has a great influence on key parameters such as absorbency under load and also temperature and time of the hydrogel drying. Chitosan is an amino polysaccharide which contains a large number of NH_2 and OH groups. In order to improve the adsorption capacity, modification of chitosan is important because of resulting hydrogels that are composed of natural polysaccharide and synthetic polymers with improving tunable swelling.

In view of the above, there is a need to develop hydrogels with incorporated poly-electrolytes that can act as sorbents as well as ion exchangers and help in the decontamination of wastewater accounting on possession of water solubilizing groups. In this context a chitosan–AAm hydrogel was prepared using gamma irradiation technique and applied for the sorption of the basic dye (Astrazone Blue BG-200%) as an example for cationic dye from simulated wastewater.

2. Experimental

2.1. Materials

Acrylamide, 99%, produced by Aldrich, M.wt. = 71.08, was used without any purification. Chitosan powder was supplied by Fluka chemical, acetylation degree 14% of viscosity. Average-molecular weight 70000 KDa, Fig. 1.The contaminant is the basic dye (Astrazone Blue BG-200%), molecular formula ($C_2OH_{26}N_3OCl$).

2.2. Instruments

2.2.1. Gamma radiation source

The samples were submitted to gamma irradiation (gamma cell type 4000 A from India), in air, at room temperature and in ambient humidity. The absorbed doses ranged from 5 to 30 kGy can be done at an irradiation dose rate of 5.54 Gy/s. Irradiation was carried out at the National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt.

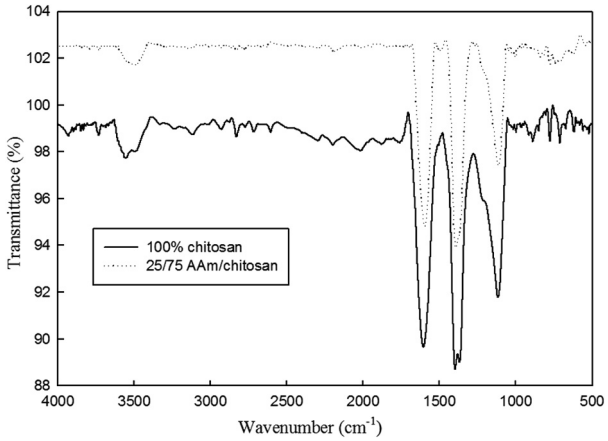


Figure 1 FTIR of chitosan/acrylamide hydrogel Wave number (cm^{-1}).

2.2.2. Infrared spectrophotometer (FTIR)

Analysis by infrared spectroscopy was carried out using Mattson 1000 FTIR spectrophotometer product of Unicam Ltd., England. About 20 mg of the sample was ground throughly with 0.2 KBr and pellets were prepared using hydraulic press under a pressure of 600 kg/Cm^2. Spectra are scanned between 4000 and 400 cm^{-1}.

2.2.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50 system, Kyoto, Japan and heated within the temperature range of 20–600 °C at a rate of 10 °C/min, under a controlled dry nitrogen flow of 40 ml/min.

2.3. Methods

2.3.1. Graft hydrogelization

Chitosan with a concentration of 1% (w/v) was prepared by dissolving 1 g chitosan powder in 100 ml bi-distilled water acidified by 1% acetic acid. Acrylamide (AAm) solution was prepared by dissolving 50 gm AAm powder in 100 ml bi-distilled water to prepare the initial concentration. At different volume ratios chitosan and AAm solutions were mixed up in samples of total volume 10 ml each, transferred into 20 cm^3 tightly closed glass tubes, and then irradiated by gamma rays.

2.3.2. Equilibrium degree of swelling (EDS)

The clean, dried, hydrogels of optimum gel content (97.7%) of known weights were immersed in distilled water at room temperature till equilibrium, and then removed from water and the excess water on the surface was rinsed, blotted by absorbent paper and weighed. The equilibrium degree of swelling (EDS) of the polymer was calculated as:

$$EDS = (W2 - W1)/(W1) \quad (1)$$

where W_2 is the weight of polymer at equilibrium (g) and W_1 is the weight of dried gel before swelling (g).

2.3.3. Gel fraction

The gel content in the dried crosslinked sample was estimated by measuring the weight of its insoluble part after extraction in distilled water till equilibrium, at room temperature. The gel fraction was calculated according to the following equation:

$$\text{Gel fraction}(\%) = (W_d/W_i) \times 100 \quad (2)$$

where W_d is the weight of insoluble part after extraction with water (g) and W_i is the weight of dried gel before extraction (g).

2.3.4. Dye removal

The effect of the chitosan–AAm volume ratio on dye removal was carried out in 25.0 ml of dye solutions (200 mg/L, initial pH 7.0) with 0.05 g of adsorbent at 30 °C for 8 h. The influence of pH on dye removal was studied by adjusting dye solutions under agitation to different pH values (4.0, 5.0, 6.0, 7.0, 8.0 and 9.0) using a pH meter (Jenway 3505). The absorbencies of dye solution were measured using a UV–vis. Spectrophotometer, Unicam UV/vis. Spectrometer (UV2), United Kingdom, at wavelength of 617 nm. Maximum amount of dye (mg) adsorbed per unit mass of the hydrogel (mg/g) was calculated by using the following equation:

$$q = V(C_o - C_e)/m \quad (3)$$

where q is the amount of dye adsorbed (mg/g), C_o and C are the concentrations of the dye in the aqueous phase before and after the adsorption period (mg/L), V is the volume of the aqueous phase (L) and m is the amount of dry hydrogel used (g).

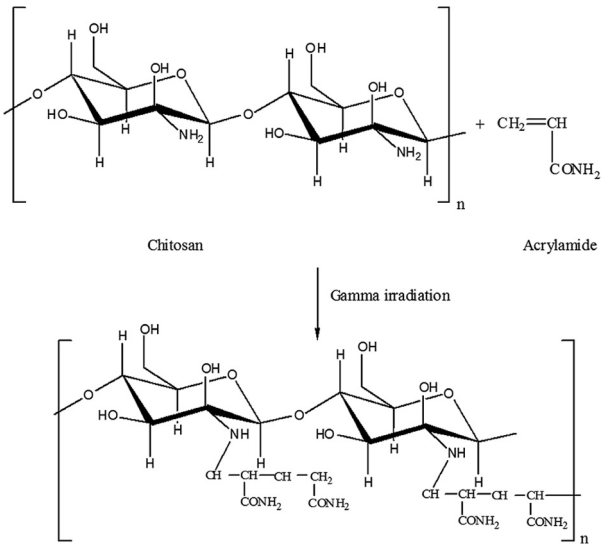
3. Results and discussion

3.1. FTIR spectra

The polymerization mechanism of acrylamide grafted onto chitosan is shown in Scheme 1. Infrared spectroscopy is a useful tool to confirm the occurrence of graft copolymerization. The FTIR spectra of chitosan and various samples of grafted chitosan–AAm are shown in Fig. 1. The IR spectrum of chitosan shows a characteristic peak of C═O around 1650 cm^{-1} due to partial deacetylation, whilst characteristic peaks of amino group appear around 3400, 1650, and 1320 cm^{-1}. For the acrylamide (AAm) adduct the overlapped peaks around 1665 and 1550 cm^{-1} were assigned to the amide I and II bands, respectively. All the above mentioned bands are common in the spectra of the graft copolymer. A new shoulder band that appeared at 3414, 1597 and 1665 cm^{-1} corresponds to –NH stretching, bending and C═O stretching vibration, respectively, thereby confirming grafting reaction. The new peak at 1560 cm^{-1} corresponding to C–N bending vibration further supports the grafting reaction.

3.2. Thermal decomposition behavior

Studies on the glass transition temperature (T_g) of chitosan are difficult to pursue because of the difficulty in sample preparation and the hydroscopicity of samples. Fig. 2 shows the TGA thermograms of chitosan–AAm hydrogel at composition 3:1,



Scheme 1 Structure of chitosan-g-acrylamide.

and irradiated polymerization at 10 kGy. It can be seen that chitosan shows the onset initial decomposition reaction at a lower temperature than chitosan–AAm hydrogel. Further, over the entire range of the applied temperature it can be inferred that chitosan polymer is thermally less stable than the prepared hydrogel. This increase in thermal stability is attributed to the grafting yield produced from pure polymers and high degree of crosslinking resulted in by gamma polymerization reaction leading to form a network structure of high crosslinking by AAm monomer. The expected results may show that the thermal stability must be much higher than the results appear in the TGA analysis of chitosan only.

3.3. Gel fraction (%)

The effect of absorbed dose on the gel% of the obtained hydrogel at different ratios of AAm is demonstrated in Fig. 3. The prepared hydrogel revealed an increase in gel fraction with increasing the absorbed dose up to 10 kGy emphasizing that

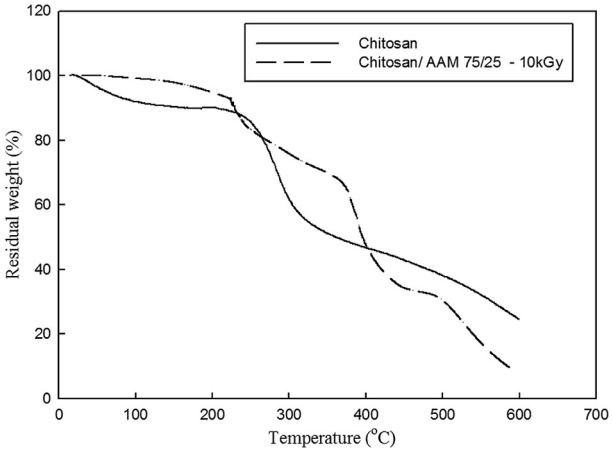


Figure 2 TGA thermograms of chitosan and chitosan/AAm hydrogel at different gamma irradiation doses.

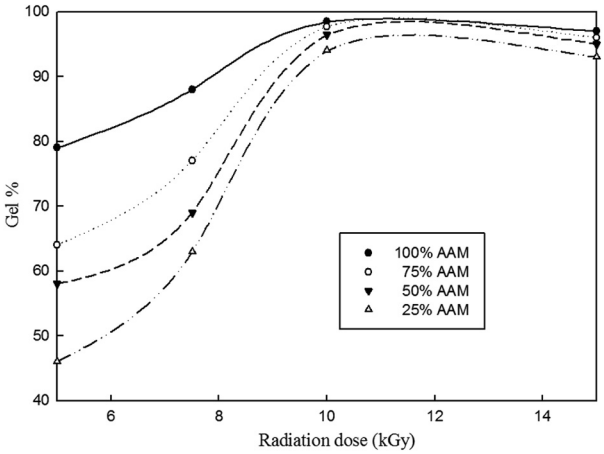


Figure 3 Effect of radiation dose on the gel % of acrylamide/chitosan hydrogel at different compositions.

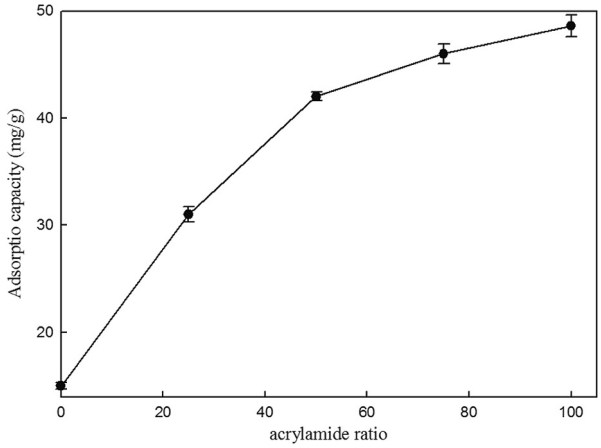


Figure 5 Effect of the chitosan:AAm (v/v)on adsorption capacity of the hydrogel for basic blue dye.

gel fraction steadily increases by increasing the absorbed dose thereof. Thereafter, gel% tends to level off complying the fact that at relatively low doses the rate of crosslinking process, hence hydrogel formation, is higher than that of the degradation process whereas at excessively higher absorbed doses, the degradation process predominates. Furthermore, the systematic increase in gel% indicates dependence on ion monomer content.

3.4. Equilibrium degree of swelling

The variation of swelling behavior of chitosan–AAm hydrogel with absorbed dose at different ratios of AAm is shown in Fig. 4. The equilibrium degree of swelling (EDS) of the prepared hydrogel steeply increased with the increase of dose until 10 kGy. This may be accounted for a progressive hydrogel formation. Within the dose range 10–15 kGy relatively lower rate of water absorption occurs due to the domination of radiation crosslinks whereas at excessive doses degradation takes place resulting in sustained reduction. Expectedly, Fig. 4 shows that the EDS of chitosan–AAm hydrogel in water increases with the increase in ionic monomer content of the hydrogel. This may be explained on the basis of the osmotic pressure exerted by the counter-ions of the AAm units. (See Fig. 5).

3.5. Removal of basic blue dye

3.5.1. Effect of chitosan–AAm ratio and absorbed dose of the hydrogel on adsorption

Chitosan-derivative, by grafting acrylamide via radiation crosslinking, was prepared and evaluated as absorbent for Astrazone Blue (a basic dye) removal. It was found that the grafting modifications greatly enhanced the absorption performance of the hydrogel (Lazaridis et al., 2007). However; the absorption capacity of chitosan–AAm hydrogel toward the basic blue dye showed a marked reduction by irradiation, Fig. 6. This can be accounted for the development of crosslinking within the absorbent, which decreases the swelling capacity of the prepared hydrogel, restricting the diffusion of the dye molecules.

3.5.2. Effect of pH value on adsorption

The dye absorption by chitosan–AAm hydrogel may be depicted by absorption transport mechanism into swollen poly-

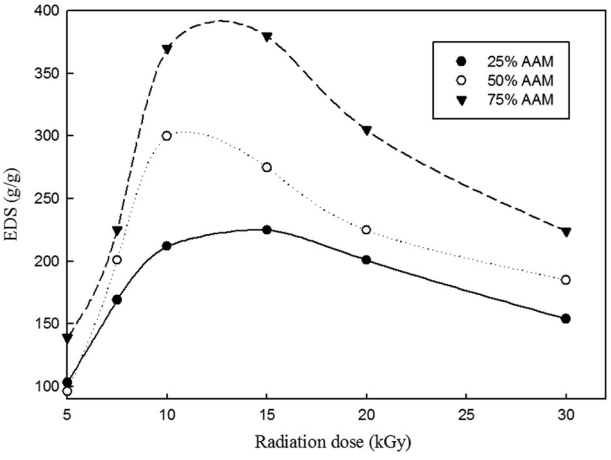


Figure 4 Effect of absorbed dose on the EDS (g/g) of chitosan/AAm hydrogel at different AAm ratios(v/v).

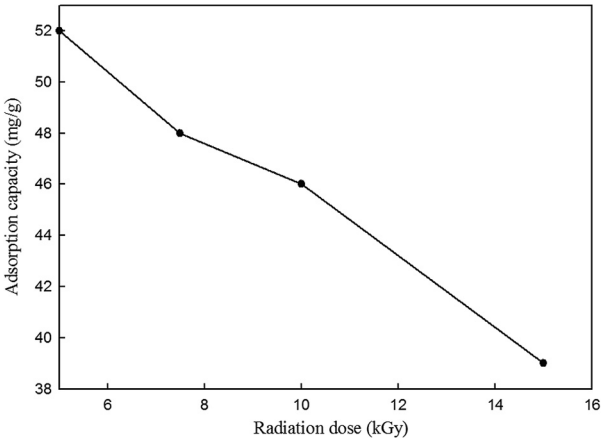


Figure 6 Effect of absorbed dose on adsorption capacity of chitosan/AAm hydrogel for basic blue dye.

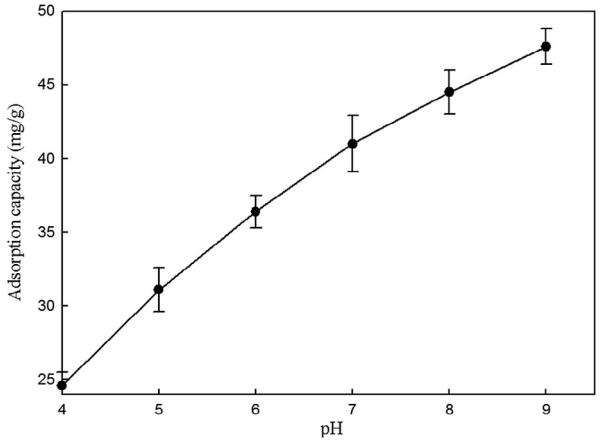


Figure 7 Effect of pH values on adsorption capacity of chitosan/AAm hydrogel for basic blue dye.

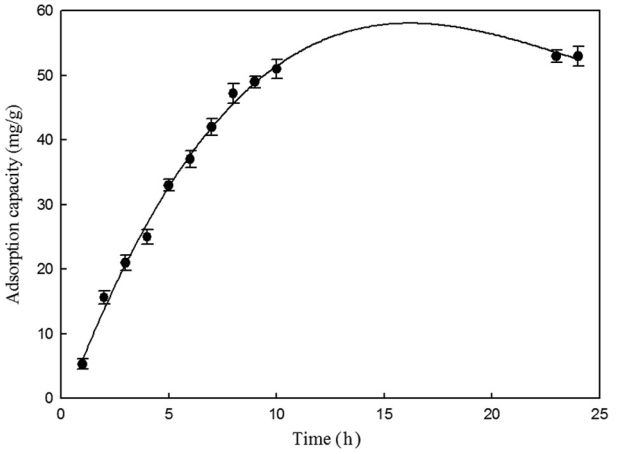


Figure 8 Effect of the adsorption time on adsorption capacity of chitosan/AAm hydrogel for basic blue dye.

mer network. The higher water content and porous structure networks allow for solute diffusion through the hydrogel structure. When a hydrogel is dipped in an aqueous medium, it begins to absorb water, resulting in considerable changes in polymer structure. The dye molecules, upon contact with water, may or may not penetrate into hydrogel depending on the established interaction between dye molecules and polymer chains. The pH of the solution affects the surface charge of the adsorbent and the degree of ionization (Bekçia et al., 2008). Fig. 7 shows the effect of pH on dye removal by chitosan–AAm hydrogel. In acidic medium (pH3), the amino groups in the chitosan–AAm hydrogels can be protonated and it was suggested that there will be a kind of electrostatic attraction between the π-electronic cloud in the basic blue dye and the absorption sites ($-NH_3^+$) of the hydrogel. Also there will be repulsion interactions present between positive charges in the basic blue and ($-NH_3^+$) in hydrogel during absorption process. This resulted in decreasing the absorption process in the acidic medium. In alkaline medium (pH = 9) the presence of the non-bonding electrons on the N atom of ($–NH_2$) group generates electrostatic repulsion forces among the adjacent ionized groups of the hydrogel network, inducing expansion of the polymer chains within the hydrogel structure. In this context, the formation of an ionic complex between basic blue molecules and chitosan–AAm network takes place, hence increasing the basic blue dye removal. The high absorption capacity is due to the strong electrostatic interaction between the negative surface of chitosan–AAm (OH) group, and the free electrons of $–NH_2$ group and the basic blue dye cation. Further, the significant absorption of the cationic dye on the adsorbent at pH above 7.0 ensures the fact that there was a chemical interaction between basic blue dye molecules and chitosan–AAm polymer. The results show that the absorption capacity of chitosan–AAm hydrogel was 47.4 mg/g of the basic blue dye at pH = 9.

3.5.3. Effect of contact time and initial dye concentration on adsorption

The effectiveness of the prepared hydrogel in adsorbing the basic blue dye has been studied as a function of agitation time and initial concentration, Figs. 8 and 9. Experimental results,

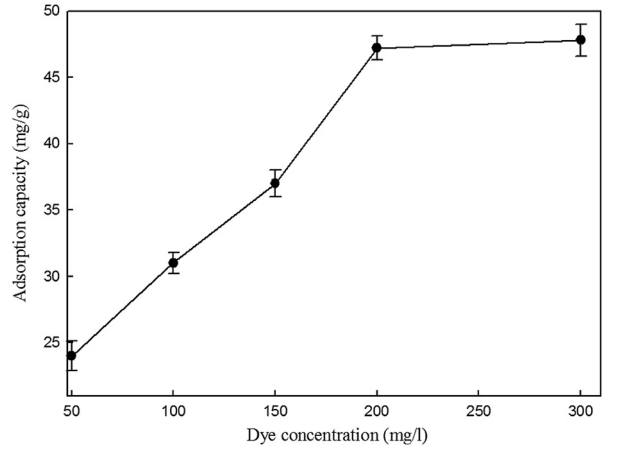


Figure 9 Effect of the dye concentration on adsorption capacity of chitosan/AAm hydrogel for basic dye.

Fig. 8, infer the strong cation-exchange character of the chitosan derivatives which was typically reported (Crini et al., 2008). The sorption of Astrazone was found to reach equilibrium within 10 h. Also, Fig. 8 manifests the influence of initial dye concentration on adsorption capacity of the hydrogel. As shown the adsorption capacity increased sharply from 24.1 to 47.2 mg/g with the increase of dye concentration from 50 to 200 mg/l, while hardly varied with further increase in dye concentration.

4. Conclusion

In the present study, we prepared a novel natural based hydrogel by graft copolymerization of acrylamide (AAm) onto chitosan. Effect of (i) chitosan–AAm ratio and absorbed dose (ii) pH of solutions on the swelling of hydrogels (iii) contact time and initial dye concentration on adsorption was investigated, results showed that the prepared hydrogels are thermally more stable than the chitosan polymer. The highest equilibrium degree of swelling of the prepared hydrogels in water, 380 g/g, was predicted at 75% AAm and absorbed dose of 10 kGy

for 97.7% gel. The application of the hydrogel for the basic dye removal from aqueous solutions revealed that the absorption capacity increases with increasing AAm content. It was found that the maximum absorption value (47.2 mg/g) was obtained at pH 9 by a hydrogel of 75% AAm irradiated by 10 kGy.

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